Influence of chemical driving forces in ion mixing of metallic bilayers

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The effective interdiffusion coefficient of metallic bilayers under ion irradiation has been correlated with the heat of mixing of corresponding binary alloys. The results are interpreted according to Darken's theory of chemically enhanced diffusion.

Ion mixing phenomena are usually described by ballistic models in which the cascade mixing is supposed to arise from collisional processes only.[1–4] However, recent investigations have suggested that thermochemical effects may be important in some cases. Large variations in mixing between systems which have similar collisional characteristics emphasize the need to take into account the chemical nature of the mixing species.[5–8] Although deviations from collisional models have sometimes been connected with so-called "spike" effects,[9] a detailed understanding of chemical mechanisms in the mixing process is still lacking.

In an effort to provide a better quantitative picture of these phenomena, we have attempted to correlate the effective interdiffusion coefficients of metallic bilayers under ion mixing with the heat of formation ΔH_m listed by Miedema for the corresponding binary alloys at the nominal 1-1 composition.[10] These values were calculated by Miedema from his well-known set of thermochemical parameters for elemental metals, which have been widely successful in the description of binary alloy formation. Moreover, the same parameters have recently been used to classify the possible locations of heavy ions implanted in Be,[11] thus providing a first indication that Miedema's approach may be relevant to ion implantation processes as well.

The systems selected for our study consisted of Pt or Au with a 3*d* metal (Ti, V, Cr, Mn, Co, Ni). Due to the similarity of their atomic number and mass, these systems are expected to behave similarly under pure collisional mixing, while covering a wide range of ΔH_m values.[10] Additionally, the large mass difference between the top and bottom layer of each couple facilitates the study of the interdiffusion process by backscattering spectrometry.

Thin bilayer films were prepared by *e*-gun evaporation in an oil-free vacuum system at initial pressures below 10^{-7} Torr. All bilayers consisted of 500 Å of Pt or Au on top of a 3000-Å-thick 3*d*-metal layer on a SiO_2 substrate. The top layer thickness was matched to the projected range of 600-keV Xe^{++} ions. The irradiations were performed at LN_2 temperature in order to reduce possible effects from radiation-enhanced diffusion; the vacuum during the irradiation was maintained below 5×10^{-7} Torr. Implanted doses were 10^{+15}, $3\times10^{+15}$, and $5\times10^{+15}$ Xe^{++} ion/cm^2 at a flux of about 200 nA/cm^2. Different samples were irradiated simultaneously to a specific dose in order to nullify possible dose and dose rate variations. An upper limit to the implanted dose was set by sputtering losses, which were moderate for Pt targets but exceeded 30% of the initial Au thickness at the highest irradiation dose. Backscattering analysis was performed with 2-MeV He^+ ions and the target tilted at 70°. Different samples were analyzed simultaneously to cancel uncertainty in tilt angle and charge integration. The observed diffusion profiles were smooth and showed no steps that would indicate the presence of a layered compound. X-ray study of mixed couples performed with a Read camera also showed no evidence of crystalline compound formation. The structure of the transition region on the atomic scale remains undefined by these experiments, but this uncertainty is of no apparent importance to our conclusion, because these relate to the chemistry of the mixing only. The high-energy edge of the backscattering signal of each bottom layer was transformed numerically to concentration versus depth profiles, assuming lateral uniformity over the mixed interface. The transformed profiles were least square fitted to complementary error functions using the interdiffusion parameter $4Dt$ as one of the fitting variables (Fig. 1). Small variations from the erfc profiles were averaged out by the fitting procedure. In fact, significant departures from that shape were only observed for a few couples (Pt-Ti, Au-Ti) at the highest implanted dose. In these cases, $4Dt$ was determined at the 1:1 concentration by a numerical Boltzmann–Matano analysis of the diffusion profile.[12] A linear relationship between $4Dt$ and the dose was fitted by linear regression analysis (Fig. 2), as suggested by current cascade mixing models and previous experimental evidence.[1–4] The slope of each line ($4Dt/\phi$) characterizes the mixing rate of each bilayer. This slope is plotted against the corresponding heat of mixing value in Fig. 3. There exists a striking correlation between both parameters. The contribution from collisional cascade mixing to $4Dt/\phi$ can be roughly estimated by calcu-

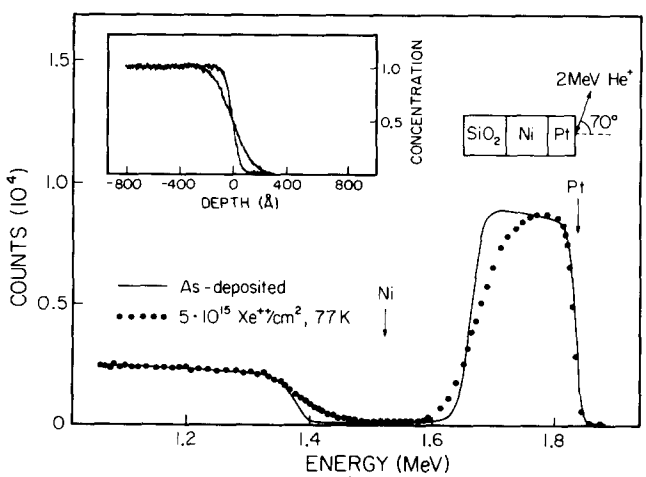

FIG. 1. Backscattering spectrum of a Pt-Ni bilayer before and after ion mixing at 77 K. The insert shows the Ni signal transformed to a concentration vs depth profile.

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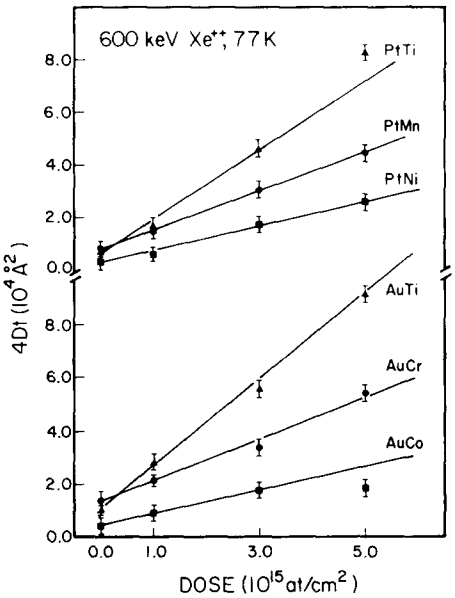

FIG. 2. Variance of interface profile vs dose for selected bilayers irradiated with 600 keV Xe^{++} at 77 K.

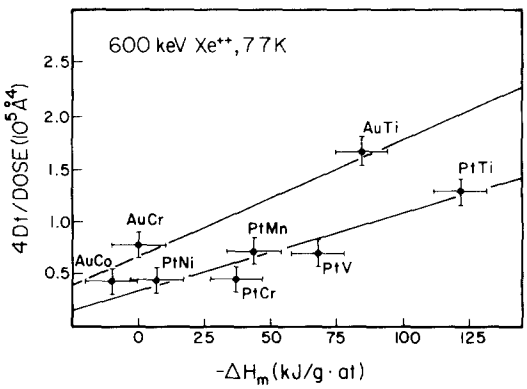

FIG. 3. Correlation between mixing parameter and Miedema's heat of mixing for various bilayers irradiated with 600 keV Xe^{++} at 77 K.

lating the effective interdiffusion coefficient due to pure collisional random walk processes, following, for example, the treatment given in Ref. 1. Considering the similar displacement energies in $3d$ elements of interest,[4] it can be verified that collisional processes cannot account for more than a 20% variation in the observed D, whereas the actual values vary by a factor of 4 for the systems under consideration. Roughening of the film surface due to sputtering effects can also affect the slope of the backscattering edge, but it is not expected to depend on the nature of the bottom layer.

To explain these results, we suggest a mixing model based on Darken's analysis of chemical interdiffusion coefficients in random regular solutions.[12–14] Taking ΔH_m as the origin of the chemical driving force for diffusion, the Darken effect can be expressed as

$$D = D_0(1 - 2\Delta H_m/RT).$$

Application of Darken's analysis to our ion mixing results implies that mixing takes place in a region where a uniform energy distribution has been established over the diffusing atoms, since the energy contained in the primary cascade has to be diluted over a large number of particles before bulk chemical forces can come into play. Moreover, energy fluctuations in this ensemble should be lower than average interatomic potential energies such as not to destroy the chemical biasing of the random walk process. Within this picture, we identify D with the effective interdiffusion coefficient around 1:1 composition, D_0 with the diffusion coefficient for pure random walk mixing, and interpret $\frac{3}{2}kT \equiv E(av)$ as the average kinetic energy per particle involved in the mixing process. A linear relationship between mixing rate $4Dt/\phi$ and ΔH_m is then predicted. From the slope we deduce $E(av) = 1.9$ eV for the Au couples and 1.3 eV for the Pt couples. This interpretation implies that the values of the heat of mixing parameters defined by Miedema remain valid in the highly energetic cascade volume. This is probably true since the matter density inside the cascade is unlikely to differ much from that of the corresponding liquid state. If our interpretation is correct, these results provide an experimental estimate of the average kinetic energy of atoms involved in the mixing process.

Applied strictly, Darken's diffusion analysis predicts a concentration profile that differs from the erfc assumed in our analysis. The treatment sketched here thus addresses only the basic features of the model. Note that marked deviations from a linear Dt vs ϕ behavior occur at high dose for systems with the largest negative (Pt-Ti) and positive (Au-Co) heat of mixing (see Fig. 2). This kind of behavior points towards either (i) a concentration dependence of D, which follows directly from the Darken effect, or (ii) a role of the heat of formation released or absorbed during mixing on the degree of mixing. Moreover, our results show a systematic difference in the amount of mixing of couples with Au and with Pt, which is probably too large to be accounted for by collisional processes.

In summary, we have observed a relationship between Dt/ϕ for binary metallic films and Miedema's heat of mixing ΔH_m. A thermochemical model of ion mixing based on a chemically biased random walk process can explain this relationship. Our results suggest that these effects plan an important role when the average kinetic energy per particle involved in the mixing process becomes comparable to their heat of formation. Since the latter is typically of the order of 1 eV, this situation must prevail in the late stages of the mixing process. Note also that according to the present model, binary systems with large positive heat of mixing are predicted to exhibit uphill diffusion, i.e., phase separation. Finally, a meaningful application of Darken's analysis precludes the existence of strong energy density gradients across the mixing interface; it also implies that energy fluctuations should be small over typical atomic diffusion lengths. It would be interesting to test these conditions under different cascade regimes by varying the mass of projectile and target atoms.

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